

# **Distribution and Cycling of Dissolved Organic Carbon and Colored Dissolved Organic Carbon on the West Florida Shelf**

Dr. Paula Coble  
College of Marine Science  
University of South Florida  
140 7<sup>th</sup> Ave South  
St. Petersburg, FL 33701  
phone: (727) 553-1631 fax: (727) 553-1189 email: [pcoble@marine.usf.edu](mailto:pcoble@marine.usf.edu)

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## **LONG-TERM GOALS**

The long-term goal of this project is to determine sources, sinks and dynamics of Colored Dissolved Organic Matter (CDOM) optical properties on spatial and temporal scales relevant to physical/biogeochemical/optical modeling efforts on the West Florida Shelf. Predictive capability is needed for modeling in-water light attenuation and visibility in coastal regions. CDOM is one of the most significant and least understood light attenuating components, hence improved understanding of its optical properties, dynamics and spatial and temporal variability will result in improved radiance models in the littoral zone.

## **OBJECTIVES**

The short-term goals are to characterize spatial and temporal variability in optical properties by determining sources and sinks of CDOM and Dissolved Organic Carbon (DOC) for the West Florida Shelf. The loss of CDOM by dilution/physical mixing and photobleaching will also be investigated. Photodegradation rates and effects of sunlight on CDOM optical properties and CDOC/DOC relationship as a function of CDOM source will be determined. This information will be applied to bio-optical and predictive light field models.

## **APPROACH**

We propose to characterize spatial and temporal variability in optical properties and relative importance of the various sources and sinks of CDOM and Dissolved organic carbon (DOC) in the ECOHAB (Ecology of Harmful Algal Blooms)/HYCODE study area on the West Florida Shelf (between 27.5° - 25.0°N, 81° - 84° W, or roughly between Tampa Bay in the north to Florida Bay in the south and 120 miles offshore). Sources to be studied include phytoplankton (diatoms, dinoflagellates, *Trichodesmium* spp.), rivers (Hillsborough, Manatee, Alafia, Caloosahatchee, Peace and Shark Rivers), and sediments. We will also investigate loss of CDOM by dilution/physical mixing and photobleaching. Photodegradation rates and effects of sunlight on CDOM optical properties and CDOC/DOC relationship as a function of CDOM source will be determined. Analyses will include:

- Detailed surface mapping of CDOM and chlorophyll fluorescence using SAFire, and DOC concentration.

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- Discrete absorption and fluorescence samples of vertical distributions on the shelf.
- Laboratory incubations of water samples using a solar simulator with subsequent measurement of DOC concentrations and CDOM fluorescence and absorption.

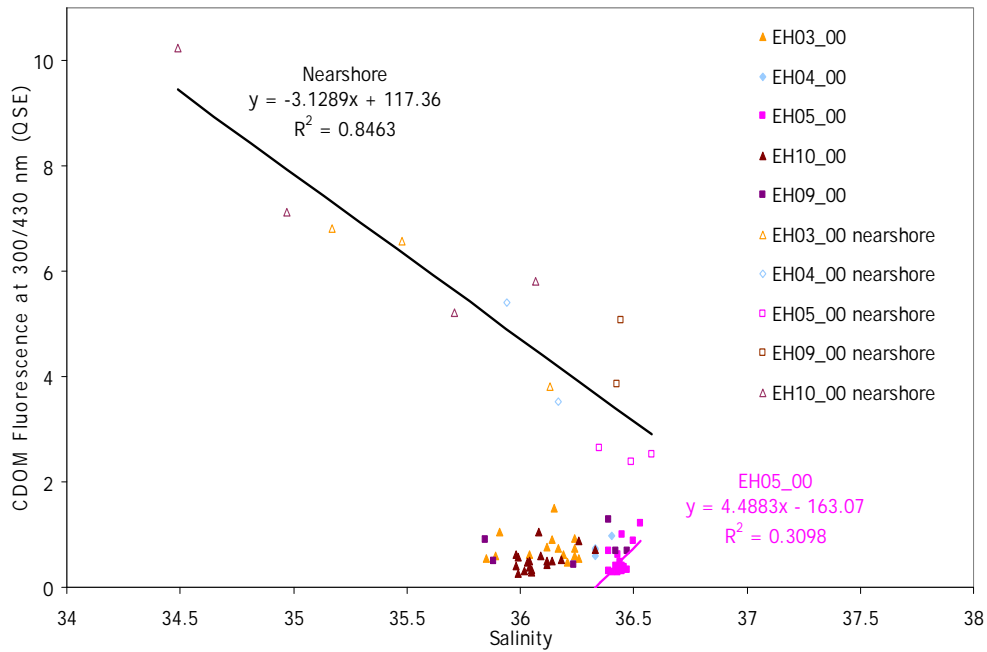
## **WORK COMPLETED**

Since the beginning of this project in 1998, we have collected more than 1,000 samples from 34 cruises in the region between the Mississippi River and the Florida Keys. The project is in the final phase of analysis of regional, seasonal, and interannual variability. In the past year, analysis has concentrated on a series of 19 ECOHAB cruises to the West Florida between October 1998 and November 2001.

## **RESULTS**

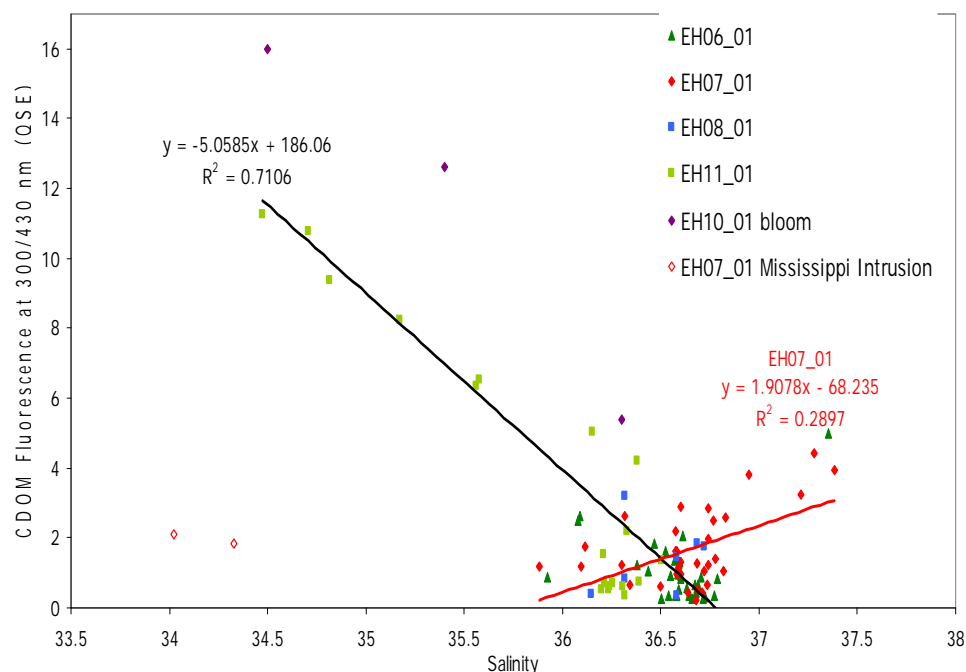
The study region extended from Tampa Bay south to Florida Bay and up to 50 mi. offshore. Salinity ranged between 31.5 and 37.5. CDOM ranged between 0.2 and 20 ppb. CDOM concentrations were highly variable and CDOM optical properties varied both temporally and regionally. Upwelling conditions resulted in positive CDOM-salinity relationships during brief periods in limited regions, and may provide a source of CDOM that is of marine, not riverine, origin. CDOM distribution on the West Florida Shelf is controlled by mixing of fresh and marine waters, where as DOC is not. Other general conclusions about results from this study period are the following:

1. Dry season and drought years (2000) are characterized by high fluorescence efficiencies due to photobleaching. During drought years, freshwater influence disappears in surface waters offshore, such that CDOM salinity mixing relationships no longer pertain (Fig. 1).



**Figure 1. Graph of CDOM fluorescence versus salinity for West Florida Shelf during 2000, showing a linear relationship for concentrations between 2 and 10 QSE and salinities between 34 and 36.5 at nearshore stations. At offshore stations, CDOM concentrations ranged between 0.2 and 1.5 QSE for salinity between 35.8 and 36.5 with no correlation to CDOM.**

2. Elevated CDOM concentrations were observed in association with red tide blooms in October 1999 and 2001, but fluorescence efficiencies were not effected.
3. Rivers in northern Florida have lower CDOM concentrations than those in the west central and southwest regions.
4. Mississippi River water is present along the west Florida shelf in very wet years (1998 - 1999). Its presence can be recognized by anomalously low CDOM concentrations and low fluorescence efficiencies.
5. High CDOM, high salinity water masses have been observed on several occasions. The two likely sources are the hypersaline waters of Florida Bay and coastal upwelling of near-bottom waters along the shelf in the region of Charlotte Harbor. The coastal upwelling was observed in all three years of the study (Dec 1999, May 2000, July 2001), in different seasons and in both wet and dry years. Thus, this source of CDOM is not dependent on rivers, but rather on the larger wind-driven circulation on the shelf.



**Figure 2. Graph showing CDOM fluorescence versus salinity on the West Florida Shelf during 2001. A negative correlation was found for all CDOM concentrations except during July when a positive relationship was observed for CDOM concentrations between 0.2 and 4 and salinities between 36 and 37.5.**

6. Correlation between CDOM and DOC was found under two conditions. The first is during red tide bloom conditions and therefore the source of CDOM is autochthonous. The second is during periods of high freshwater runoff. Correlations were better for CDOM measured as  $a_{250}$  than as fluorescence or as absorbance at any other wavelength.

7. Fluorescence efficiencies at fluorescence =  $E_x/E_{m300/430}$  and  $a_{440}$  ranged from 23 during wet seasons to 30 during dry seasons. In all, the fluorescence efficiencies were fairly stable and fluorescence can be used as an accurate substitute for absorbance even during periods of Mississippi River water intrusions.

## IMPACT/APPLICATIONS

CDOM is one of the most significant and least understood light attenuating components in the ocean, hence improved understanding of its optical properties, dynamics and spatial and temporal variability will result in improved radiance models in the littoral zone. A major objective of this study is provide data for development and validation of coupled physical/ecological/bio-optical models which will incorporate phytoplankton, CDOM, suspended sediment distributions into models to account for hyperspectral water-leaving radiance  $L_w(\lambda)$  and inherent optical properties (IOPs) fields. Data collected from this project will be used to generate detailed surface mapping of CDOM fluorescence and absorption, and DOC concentrations on the West Florida Shelf. Hence, this information will prove useful in improving bio-optical and predictive light field models.

## **TRANSITIONS**

We have a good understanding now of seasonal and spatial variability of CDOM on the West Florida shelf. The largest source of variability is due to variability in freshwater inputs from coastal rivers. Since the CDOM concentrations of these rivers is also highly variable, the next step towards improved understanding is to study the individual rivers and begin modeling CDOM inputs on the scale of watersheds and basins. Such observations coupled with soil runoff and erosion models will further advance understanding and modeling of CDOM dynamics in coastal regions.

## **RELATED PROJECTS**

During the course of this project, we have worked collaboratively with several programs including HYCODE/ONR (Carder, USF), ECOHAB (Vargo et al., USF and Heil, FWC), and on-going SeaWiFS and MODIS ocean color studies on the West Florida Shelf (Muller-Karger and Hu, USF).

## **PUBLICATIONS AND PRESENTATIONS**

Coble, P.G. 2007. Marine Optical Biogeochemistry – The Chemistry of Ocean Color. *Chem. Rev.* 107: 402-418.

Conmy, R.N., P.G. Coble and C. Heil. 2007. Seasonal Variations in CDOM on the SW Florida Shelf: Spectral Properties and Distribution Patterns. Winter ASLO Meeting, Santa Fe, NM Feb. 5-9, 2007.

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Murphy; Kathleen, William T Dunsmuir; Gregory M Ruiz; David T. Waite; Paula G.Coble. 2007. The stability of dissolved organic matter fluorescence in frozen seawater samples. *Water Research* (submitted)